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6. AUTHOR(S)
Robert A. Osteryoung

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
State University of New York at Buffalo
Department of Chemistry
Buffalo, NY 14214

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Electrochemical studies on the reduction of $AlCl_4^-$ion and the anodization of Al(0) in basic 1-methyl-3-ethylimidazolium chloride (ImCl) mixed with aluminum chloride ($AlCl_3$) were carried out; a basic melt is one containing excess ImCl. It was not found possible to reduce the $AlCl_4$-ion at temperatures as high as 250°C. The anodication of aluminum was found to be controlled by the diffusion of chloride ion to the electrode. The disposition of Li and Bi were studied at tungsten microelectrodes in LiCl-KCl eutectic molten salt at 450°C.

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FINAL REPORT

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STUDIES OF COMPONENTS FOR THERMALLY REGENERATIVE ELECTROCHEMICAL SYSTEMS

Robert A. Osteryoung

Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

This work was supported by SDIO/IST and managed by ONR.

Objectives

The objective of this research was, initially, to study the chemistry and electrochemistry of components to be utilized in the development of a thermally regenerative electrochemical system (TRES). The original work was aimed at exploring the use of ambient temperature ionic liquids (molten salts), consisting of an organic halide mixed with aluminum halide, as potential electrolytes for a TRES system. The objective was later changed to study electrochemistry in a high temperature molten salt, a lithium chloride-potassium chloride eutectic, in support of pulse power battery applications.

Technical Approach

Our initial work utilized an ambient temperature molten salt consisting of 1-methyl-3-ethylimidazolium chloride (ImCl) mixed with aluminum chloride ($AlCl_3$). This solvent system is characterized as acid, basic, or neutral, if the mole ratio of $AlCl_3$ to ImCl is greater than, less than, or equal to unity, respectively. The Lewis acidity of the solvent is varied by changing the system acidity; this is accomplished by varying the mole ratio of $AlCl_3$ to ImCl. Our initial goal was to determine if it were possible to reduce the $AlCl_4^-$ in a basic melt by raising the temperature; Al(0) can be deposited from an acidic melt, and the thought was that it might be possible to arrive at a concentration cell of reasonable voltage that could be thermally regenerated. A program redirection was obtained to permit studying reactions in higher temperature, potassium chloride-lithium chloride eutectic melts at very small electrodes; this work was related to the development of high powered pulse batteries.

Results

Efforts to reduce the $AlCl_4^-$ anion in a basic $AlCl_3$-ImCl melt at temperatures up to 250°C were unsuccessful. The anodization of Al(0) was studied in the basic $AlCl_3$-ImCl melt. The anodization process was studied as a function of chloride anion concentration. Two different anodization processes were observed with onset potentials, against the Al-Al(III) reference, of -1.1 and 0 V. The more negative anodization involved formation of the tetrachloroaluminate anion and exhibited a limiting current controlled by diffusion of chloride to the electrode surface. The number of chlorides required fro each Al anodized was determined to be 4.6 ± 0.4. The more anodic process showed no diffusion control. Tungsten ultramicroelectrodes were employed to examine the cathodic and anodic limits of a basic melt. Staircase cyclic voltammetric scans were performed well beyond the normal melt electrochemical potential limits. In the cathodic region, reduction of the Im^+ was clearly seen at -2.3 V, and another, unknown reduction process at -5.5 V was also observed. In the anodic region, oxidation of both Cl^-, at 1.3 V, and

$AlCl_4^-$, at 3.0 V, were also observed. From normal pulse voltammetry, diffusion coefficients of Im^+ and Cl^- were determined.

As a sidelight of this study, some work was carried out on the electrochemistry of the molybdenum(III) dimers, $Mo_2Cl_9^{3-}$ and $Mo_2Cl_8H^{3-}$, and the molybdenum(II) dimer, $Mo_2Cl_8^{4-}$, in basic melts. The scheme for the electrochemical processes that the dimers undergo was deduced.

Since it was felt that the results obtained were unsatisfactory as far as the initial goals of the project were concerned, and change in direction to examine Li metal deposition in a LiCl-KCl eutectic molten salt was requested and obtained. Tungsten ultramicroelectrodes were employed to study both the deposition and stripping behavior of Li/Li^+ and Bi/Bi^{3+} in the LiCl-KCl eutectic melt at 400°C. The Li deposition current could be simulated assuming the growth of a single hemisphere of liquid metal on the microelectrode. High stripping current densities were observed and quantized using standard electrochemical equipment, possible because thought the current densities were very high, the absolute magnitude of the current was small. An inverted microscope assembly was employed for *in situ* observation of the Li/Li^+ deposition and stripping processes at the microelectrode.

Publications

"Electrochemistry of Molybdenum Dimers in a Basic Ambient-Temperature Molten Salt", Richard T. Carlin and Robert A. Osteryoung, Inorg. Chem., **1988**, *27* 1482.

"Microelectrodes in the Examination of Anodic and Cathodic Limit Reactions of an Ambient Temperature Molten Salt", Richard T. Carlin and Robert A. Osteryoung, **1988**, *252* 81.

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"Aluminum Anodization in a Basic Ambient Temperature Molten Salt", Richard T. Carlin and Robert A. Osteryoung, J. Electrochem. Soc., **1989**, *136* 1409.

Individuals (Technical) Supported on Grant

Dr. Richard T. Carlin
Dr. John Sanders
Dr. J. O'Dea
Mr. Sinru Lin